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AZ0 POLYMERS FOR REVERSIBLE OPTICAL STORAGE 3.

EFFECT OF FILM THICKNESS ON NET PHASE RETARDATION AND WRITING SPEED.

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Abstract

The optical writing phenomenon observed on azoaromatic containing polymer thin films exhibited a writing rate which was proportional to the intensity of the writing beam. This property of the mechanism for optically inducing dichroism and birefringence directly results in non-linear optical behavior in the thin film. The net phase retardation obtainable and writing rates are functions of the thin film thickness which reflect this nonlinear behavior.

Introduction

In recent years there has been an increased interest in the use of photopolymers for optical holography, optical information storage and integrated optics[1-4]. Optical information can be written, read, erased and rewritten on amorphous polymer films containing azobenzene groups[5-7]. The information is encoded by optically inducing dichroism and birefringence on small spots. The induced change has been shown to have long term stability and can be read with minimal perturbation. Among the properties of interest are the net phase retardation due to birefringence and the writing rate. These are of interest both to understand and quantify the phenomenon involved as well as to implement the use of these films in optical storage devices.

As pointed out in an earlier paper[6], the mechanism for writing involves the photochemical excitation of the azobenzene group which undergoes a trans-cis isomerization and then relaxes back to the trans state after some reorientation. The rate of cis-trans isomerization is fast on the time scale of our experiments[8]. We thus consider that the effect of light absorption is to reorient of the trans state. By repeating these trans-cis-trans isomerization and reorientation cycles a substantial portion of the initially homogeneous distribution of the azobenzene groups becomes aligned perpendicular to the laser polarization direction. This reorientation is measured by monitoring the birefringence of the film. The characteristic time required for the chromophores to exhibit a net asymmetry in their orientational distribution is inversely proportional to the intensity of the writing beam[6], this reflects the number of cycles required to reorient the molecules.

In order to achieve high writing efficiency, one normally selects light which is readily absorbed by the trans state of the chromophore. This should decrease the writing time since more photons are absorbed per second leading to more reorientation cycles. On the other hand, the high absorption efficiency also means that the intensity of the writing beam rapidly decreases as a function of depth into the specimen, thus the trans-cis-trans cycling rates will now decrease as a function of depth into the specimen. Furthermore, since the writing beam also induces dichroism by reducing the number of chromophores which can absorb the light, one can expect the coefficient of absorption to decrease with time. The fact that the transition rate depends on intensity and that dichroism is induced leads to optical nonlinear behavior in the film.

In the present paper the effect of the nonlinear absorption properties on the writing times and efficiencies is investigated as a function of the sample thickness. The probe beam monitors the birefringence induced in the film. The wavelength of the probe is selected to be outside the main absorption band of the dye such that the beam is not absorbed in the film and does not itself induce molecular reorientation. Although we present results on a specific polymer film, similar results can be expected in analogous optical systems which show nonlinear optical effects.

Experimental

The measurements reported here were obtained on ***pDRIA*** polymer thin films prepared as previously described [6,7].

The polymer was dissolved in tetrahydrofuran (THF) and films of varying thicknesses were cast onto clean glass slides which acted as transparent substrates. The thickness of the films was estimated by measuring the displacement of interference fringes produced by light reflected from the film surface with respect to those produced by light reflected from the substrate. A second check was performed by measuring the initial transmission of the films for unpolarized light, and assuming that the absorption coefficient is sample independent, relative thicknesses could be computed.

A linearly polarized Argon laser beam at **514.5** ***nm*** was used to write on the films. The writing beam was set at a power of **4** ***W/cm²***. The optical recording was monitored by measuring the net phase retardation of the film at **632.8** ***nm*** with a weak **1** ***mW/cm²*** ***HeNe*** probe beam as described previously[5].

Results and Discussion

A typical example of the optically induced dichroism is presented in Figure 1. This dichroism has be observed to be stable over extended periods of time (in excess 2 years) and can be erased by writing on the spot with random or circularly polarized light. There appears to be no significant shape difference between the three spectra indicating that the mechanism responsible for the dichroism is a reorientation of the trans azo molecule. This result is consistent with fast cis-trans photo or thermal isomerization.

From a Kramers-Kronig (K-K) analysis of these spectra we can estimate the birefringence expected at the probe wavelength. This is given by.

$$\Delta n\ (w_p) = \frac{c}{\pi}\ P \int_0^{\infty}\ \frac{\Delta \alpha\ (w)}{w^2 - w_p^2}\ dw \qquad (1)$$

where $\Delta n\ (w_p)$ is the birefringence, $\Delta \alpha\ (w)$ is the change in absorption coefficient.

The K-K analysis gives $\Delta n = .074$ at **633nm** and we have measured $\Delta n = .071$. As well the K-K analysis gives $\Delta n = .057$ at a probe wavelength of **750nm** and we measure **.056**. The optically induced phase retardation was measured on many samples as a function of time. Figure 2 presents typical results obtained on samples of increasing thickness : **55, 118, 160, 260**, and **350** nm. These results illustrate two of the basic features which are a consequence of the nonlinear behavior of the writing mechanism. As the sample thickness increases the writing intensity can vary substantially throughout the sample as a consequence, the effective writing time to reach saturation of the birefringence throughout the film increases dramatically. For films which are thin compared to the writing light penetration depth, the saturation level increases linearly with thickness. On the other hand for thick samples complete saturation is not acheived in the finite experimental time.

The above results can be interpreted to be a consequence of the optically induced dichroism and the intensity dependence of the molecular reorientation rate. As an example of this behavior consider the following case. A writing beam which is absorbed in a polymer film causes molecular reorientation such that the local absorbtion coefficient, α, in the film is a function of both depth, x, and time, t.

The rate of change of the absorption coefficient can be described by

$$\frac{\partial \alpha(x,t)}{\partial t} = k\ (\alpha(x,t) - \alpha_{\infty})I(x,t) \qquad (2)$$

where it is assumed that the rate of change is proportional to the local intensity of the writing beam $I\ (x,t)$, that the absorption coefficient will eventually saturate to a value α_{∞}, and k, is a constant representing the efficiency of the beam to induce molecular re-orientation and includes effects such as quantum yield of isomerization and angular diffusion rates.

The local intensity of the writing beam can be described by

$$\frac{\partial I(x,t)}{\partial x} = -\ \alpha(x,t)\ I(x,t) \qquad (3)$$

which when coupled with equation (1) can be used to illustrate the non-linear optical behavior. We now assume that the absorption spectrum does not change shape but that dichroism as illustrated in Figure 1 is being generated. The phase retardation of the film is then calculated as

$$\phi = C\int_{o}^{d} (\alpha(x,t) - \alpha_{o})\ dx \qquad (4)$$

where C is a proportionality constant, α_{o} is the absorption coefficient of the homogeneous film, and d is the thickness of the film.

Figure 3 presents a computer solution of equation 3 for varying thicknesses $\alpha_o d = .5, 1, 2, 4, 8, 16$ with $\alpha_- \approx .8\alpha_o$. This simulation reproduces very well the general features of the data, confirming the origins of the effects seen. When the film thickness exceeds $4/\alpha_o$, the initial writing dynamics becomes independent of the thickness and the excess thickness of the film does not participate in the optical recording to any significant degree since the intensity of the writing beam is small in that region. In the present case this break should occur at an approximate thickness of $d = 4/\alpha_o \approx 320nm$ in qualitative agreement with figure 2. An even more critical consequence of the film thickness is the significant increase in writing times for thick films resulting from the decrease in intensity of the writing beam as it penetrates into the sample.

We have not attempted to analyse the curves in figure 2 in any great detail. The theory presented above does not lend itself to straightforward analysis since the resulting data exhibits nonlinear behavior. We have assumed in the above illustration that the writing time exhibits one characteristic rate while the actual data, even for very thin samples exhibits at least two rates thus making the analysis of thick samples even more difficult and of limited value.

From the results and analysis presented in this paper it is clear that intrinsic time constants can be more readily obtained by analyzing films which are thin in comparison to the inverse of the absorption coefficient. Furthermore when considering possible applications for these optical recording material, optimum design criteria should incorporate the effects of film thickness on writing time and efficiency.

Acknowledgements

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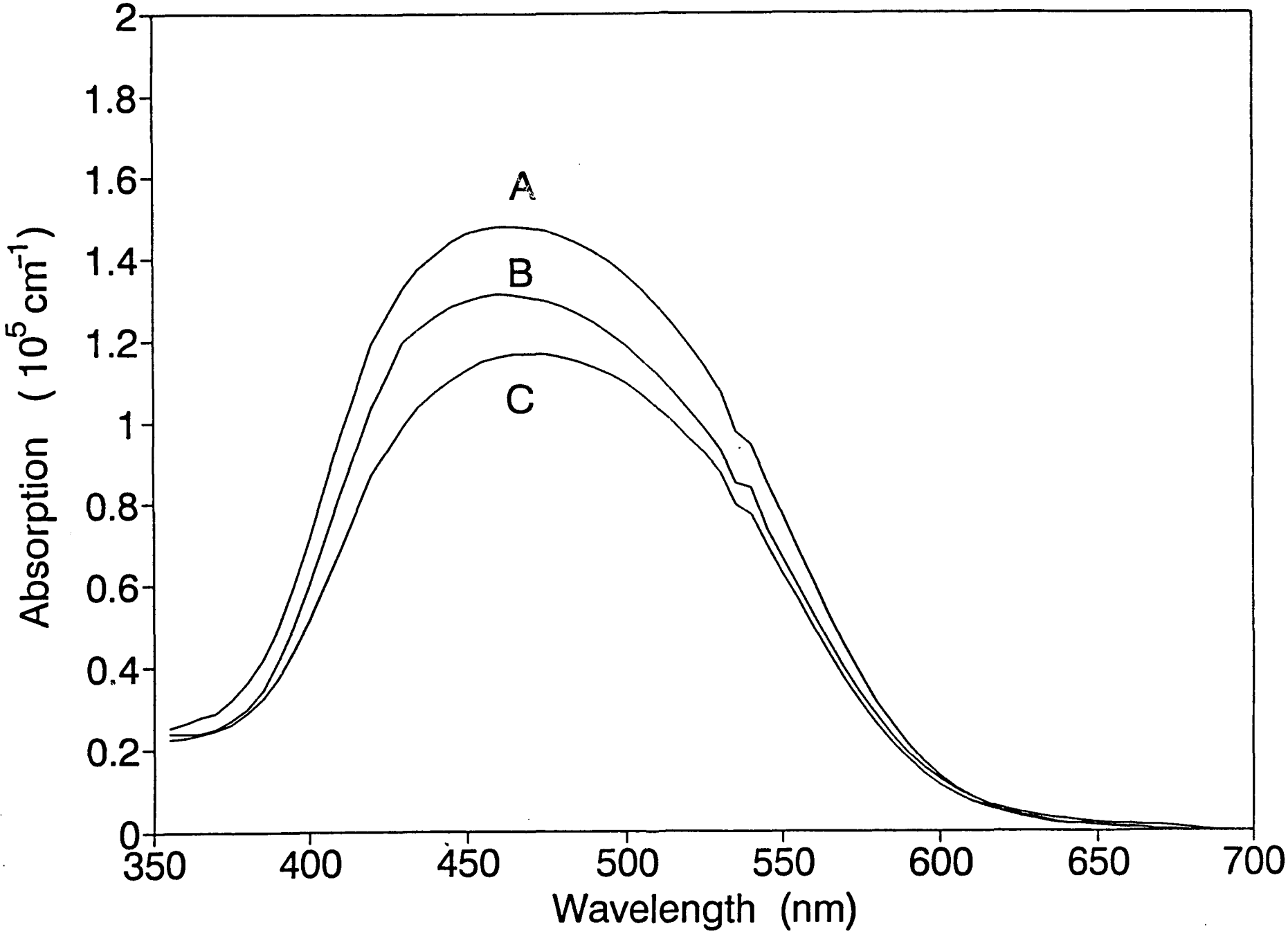
Figure Captions

1. Absorption spectra of ***pDRA1***. B: not written, A: perpendicular to writing polarization, C: parallel to writing polarization.

2. Induced phase retardation on ***pDR1A*** films as a function of time. Film thicknesses are ***A*: 55 *nm*, *B*: 118 *nm*, *C*: 160 *nm*; *D*: 260 *nm*; *E*: 350 *nm*.**

3. Induced phase retardation simulation as a function of time for various film thickness ($\alpha_o d$) given by ***a*: .5, *b*: 1.0, *c*: 2.0, *d*: 4.0, *e*: 8.0, *f*: 16.0.**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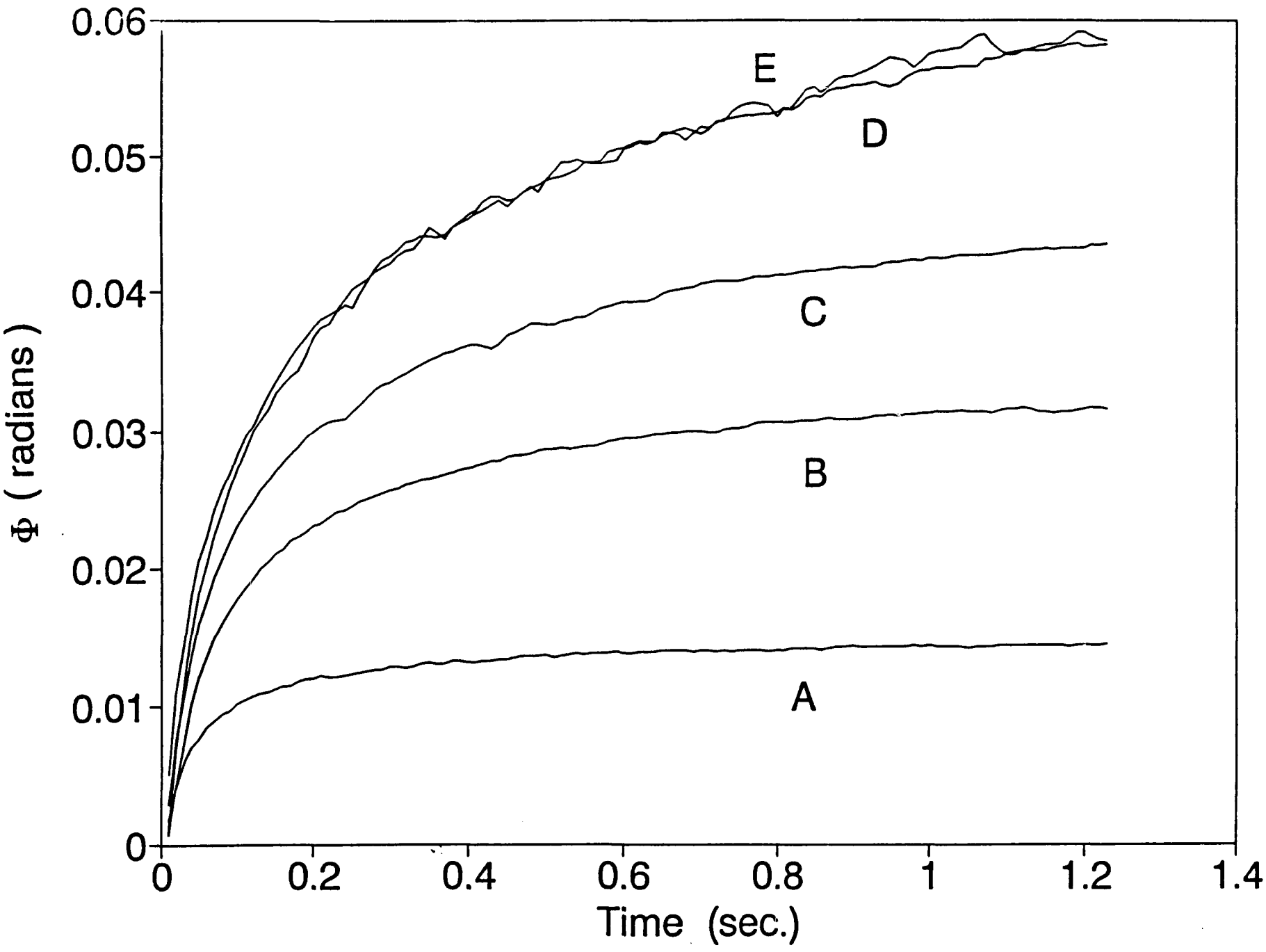
Wavelength (nm)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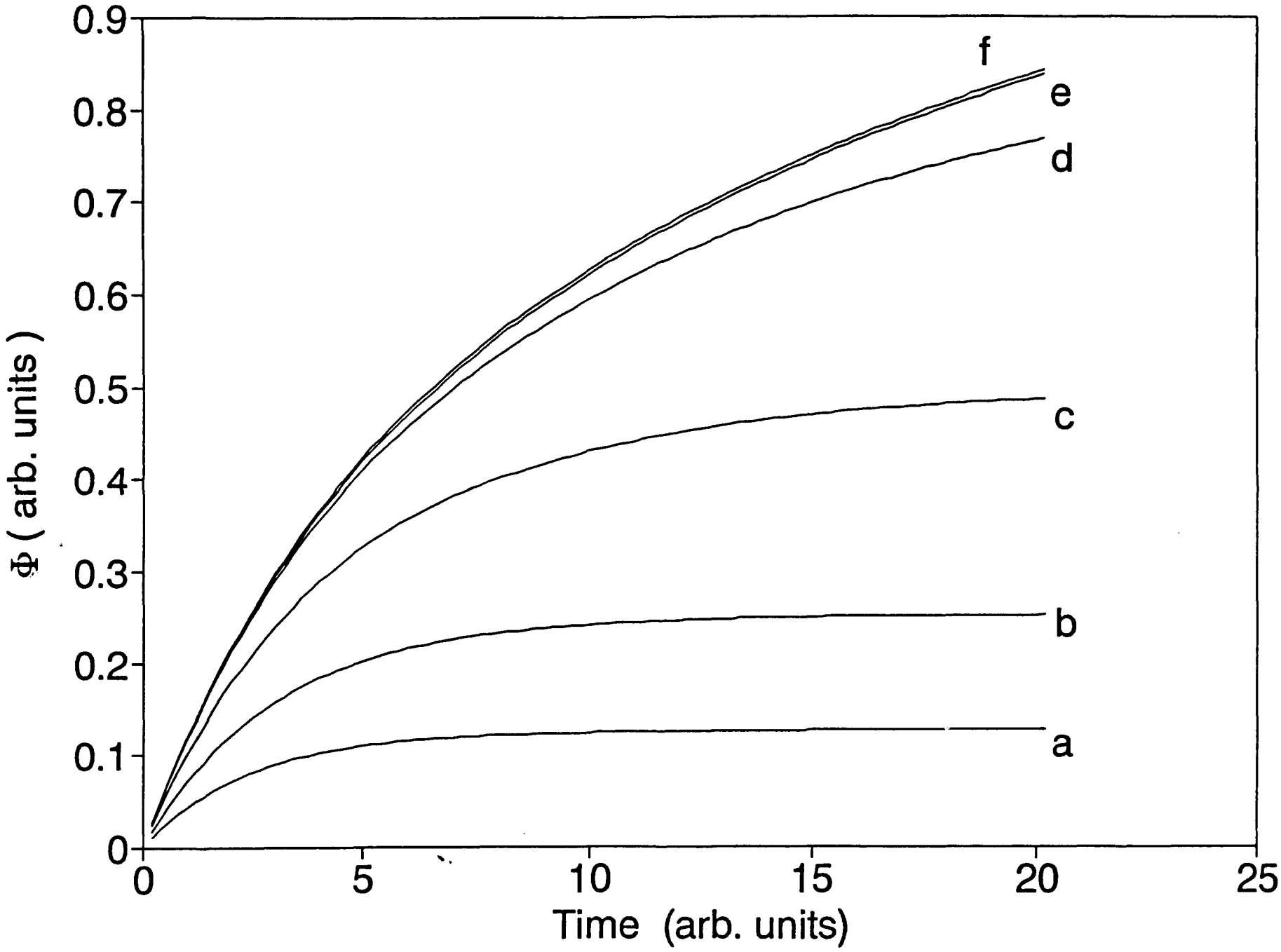
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